

SOLAR IRRADIATION USING TiO_2 FOR DEGRADATION OF ORGANIC PHOSPHOROUS PESTICIDES IN DOUBLED SKIN SHEET REACTOR (DSSR)

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TÓM TẮT

NGHIÊN CỨU QUÁ TRÌNH PHÂN HỦY THUỐC TRỪ SÂU CƠ PHÓT PHO SỬ DỤNG XÚC TÁC TiO_2 BẰNG HỆ QUANG HÓA GIÁ ÁNH SÁNG MẶT TRỜI (DSSR)

Quá trình phân hủy quang xúc tác của các thuốc trừ sâu cơ photpho như Methamidophos (Me) và Monocrotophos (Mo) được nghiên cứu trên thiết bị phản ứng 2 lớp mô phỏng ánh sáng mặt trời (DSSR). Mười hai loại xúc tác thương mại có thành phần chính là TiO_2 đã được thử hoạt tính ở các nồng độ 500 và 1000 mg/l. Sự ảnh hưởng của pH cũng được khảo sát ở các giá trị 3, 7 và 12. Kết quả nghiên cứu cho thấy, quá trình phân hủy quang xúc tác của Me và Mo trong môi trường axit ($\text{pH}=3$) và môi trường kiềm ($\text{pH}=12$) xảy ra nhanh hơn trong môi trường trung tính ($\text{pH}=7$).

1. INTRODUCTION

Recent studies have shown unsafe storage, handling, application and disposal of pesticides, which all increases the risk of incidental exposure and contamination of water canals and ducts [1, 2, 3, 4, 5]. The side effects of pesticides on humans are also linked to bronchial asthma, eye irritation, and pulmonary disorders [6]. Two very efficient organophosphorous insecticides Methamidophos (Me) and Monocrotophos (Mo) are used in great quantities worldwide and in VietNam. They possess a very high toxicity, but pose no

chronic toxicity [7, 8]. In Vietnam, these insecticides were often detected in the environment, especially in vegetables and in surface water [9]. Therefore, these two insecticides were chosen as the model compounds in this work.

Heterogeneous photocatalysis has long been discussed as an alternative method for the purification of water. A number of investigations have been made regarding the degradation of highly toxic and refractory organic compounds, as organophosphorous insecticides, chlorinated hydrocarbons and others.

Titanium dioxide (TiO_2) is a non-toxic semiconductor with the highest photocatalytic activity. It is also stable in aqueous solution and inexpensive. Therefore, the oxidative experiments with two insecticides were carried-out by using UV/ TiO_2 process in a Double Skin Sheet Reactor (DSSR). The aim of the present study were to determine the best photocatalysts among 12 different TiO_2 materials and to find a more sufficient method to accelerate the efficiency of the photocatalytic process

2. EXPERIMENTAL

2.1. Double-Skin Sheet Reactor (DSSR)

Briefly, it consisted of an UV-A light source, a light homogeniser, a reflector unit and a photoreactor with an air-sparging unit. 16 fluorescent tube-lamps of the type CLEO Performance R 40 W from Philips were mounted in a 1200 mm x 675 mm sleeve support. The front of the light source was covered with the light homogeniser (1200 mm x 600 mm x 3 mm) made of UV-A-transparent ground acryl glass to get a more homogenous and diffuse light field.

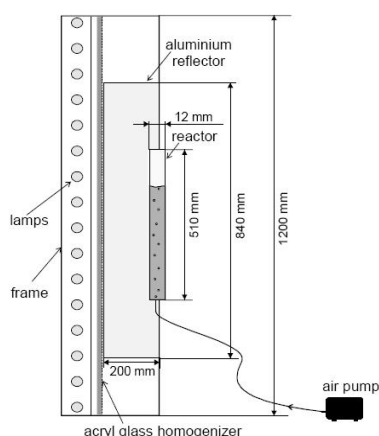


Figure 1: Double Skin Sheet Reactor (DSSR)

At the irradiated side of the photoreactor the average incident photon flux density

was measured as 22 W m^{-2} using a Dr. Hönle UV-A-meter. The local deviation of the incident photon flux density was less than 2.5%. The photoreactor was made of a polymethylmethacrylate, PMMA (Plexiglas, Röhm GmbH Darmstadt) double skin sheet (SDP 16/32) sealed on the bottom, thus forming 7 individual UV-A light transmitting rectangular tubes (510 mm x 66 mm x 12 mm). The distance between light homogeniser and photoreactor was 190 mm.

The degradation rate was calculated by multiplying this constant with the initial concentration of Me. The photonic efficiency ζ (in %) was determined as the ratio of the photocatalytic degradation rate $d[\text{Me}]/dt$ over the incident light intensity $d[h\nu]/dt$ or calculated by the following equation:

$$\zeta = (k [\text{C}_0] / I_0) * 100 \% \text{ where}$$

k is rate constant (min^{-1})

C_0 is initial concentration of Me (mM), and I_0 is incident light intensity ($I_0 = 0.084$ and $0.23 \text{ mM photons l}^{-1} \text{ min}^{-1}$ for the LSSR and DSSR, respectively) [11].

The photonic efficiency ζ was used to compare the activities of the different photocatalysts.

2.2. Photocatalytic Oxidation using DSSR

The required amount of catalyst (500 or $1000 \text{ mg l}^{-1} \text{ TiO}_2$) was put into a conical beaker, which contained the organosporous insecticide solution ($10 \text{ mg l}^{-1} \text{ Me or Mo}$). Then, the suspension was well stirred. Each of seven Plexiglas tubes of the DSSR was filled with 250 ml of the suspension. During all experiments, the photoreactor was continuously purged with

air at a rate of 35 l h⁻¹ to get a well mixed reacting medium and to guarantee a constant concentration of O₂. Samples of 5 ml were collected in regular intervals during the irradiation, centrifuged or filtered by using a syringe filter, and then taken for further analyses.

2.3. Analytic Methods

Me and Mo were determined by using a gas chromatography Fisons Instruments GC

8000 series coupled with Nitrogen-Phosphorus detection (GC-NPD).

The intermediates or by-products were determined by means of Gas Chromatography (GC) and High-Performance Liquid Chromatography (HPLC) coupled with Mass Spectrometric detection (GC-MS and LC-MS).

Table 1: Description of different TiO₂ photocatalyst powders (Cat 1-Cat 12) used

Catalyst	Name	Specification of supplier
CAT 1	P25	BET surface area: 50 m ² g ⁻¹ . Average particle size (nm): 30. Crystalline structure: Anatase/Rutile: 70 / 30 %.
CAT 2	PC 50	BET surface area: 40 m ² g ⁻¹ . Average particle size (nm): 20-30. Crystalline structure: 100 % anatase.
CAT 3	PC 100	BET surface area: 90 m ² g ⁻¹ . Average particle size (nm): 15-25. Crystalline structure: 100 % anatase.
CAT 4	PC 105	BET surface area: 85 m ² g ⁻¹ . Average particle size (nm): 15-25. Crystalline structure: 100 % anatase.
CAT 5	PC 500	BET surface area: >250 m ² g ⁻¹ . Average particle size (nm): 5-10. Crystalline structure: 100 % anatase.
CAT 6	Bayoxide-T1	BET surface area: 300 m ² g ⁻¹ . Average particle size (nm): 1. Crystalline structure: 90 % anatase, SO ₃ : ca. 0.5 %, Na ₂ O: ca. 0.05 %, Fe: ca. 0.01 %. Lost by calcination: ca. 10 %.
CAT 7	Hombikat UV 100	BET surface area: > 250 m ² g ⁻¹ . Average particle size (nm): < 10. Crystalline structure : 99 % anatase, very few amount of Fe. Volatile content 105 ⁰ C: 8 %. Lost by calcination at 850 ⁰ C: 9 %.
CAT 8	Mikro-Anatas	BET surface area: 271 m ² g ⁻¹ . Average particle size (nm): 10-20. Crystalline structure: 100 % anatase.
CAT 9	Series « H » (Lot 48)	BET surface area: 120 m ² g ⁻¹ . Average particle size (nm): 5-15. Crystalline structure: 100 % anatase.
CAT 10	P25 platinised 0.5 %	Institut für Solarenegeforschung ISFH, Germany.
CAT 11	Hombikat UV 100 platinised 0.2 %	Institut für Solarenegeforschung ISFH, Germany.
AT 12	Bayoxide-T2	Crystalline structure: Anatase TiO ₂ : 98%, Fe ₂ O ₃ < 2%.

3. SOLAR PHOTOCATALYTIC OXIDATION OF ME AND MO USING DSSR

The degradation of Me and Mo was undertaken by using the Double Skin Sheet Reactor (DSSR) and compare with Lab Solar Simulated Reactor (LSSR) and 12 different photocatalysts which were Cat 1 - Cat 12 with concentrations of 500 and 1000 mg l⁻¹. The experiments were carried-out at pH values of 3, 7, and 12.

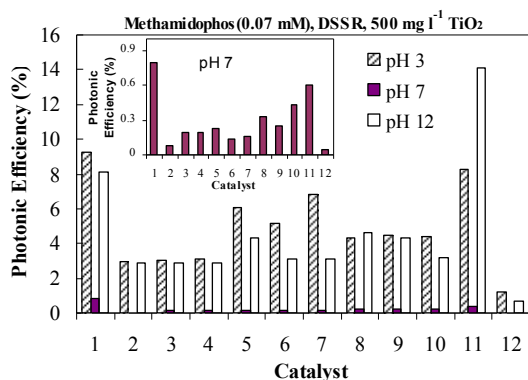
3.1. Degradation of Me: Effects of pH, catalysts concentration and type

In the photocatalytic degradation of Me using reactor Double Skin Sheet Reactor (DSSR) at pH 7 and concentration of 500 mg l⁻¹ TiO₂ (**Fig. 2a**), Cat 1 (P25) reached its largest photonic efficiency ($\zeta = 0.81\%$), exceeding that of Cat 10 (Pt-P25) and Cat 11 (Pt-Hombikat UV100). The degradation of Me using the DSSR was 1.5 to 2.5 times more efficient than that using the LSSR. For example, the half-life of the photocatalytic degradation of Me with the LSSR at pH 7 and 500 mg l⁻¹ TiO₂ was 58.7 minutes, while that with the DSSR was only 26.2 minutes. However, the photonic efficiency of Cat 1 reached with the DSSR which is 0.81%, was slightly less than that with the LSSR, which is 0.98 %. It may be interpreted from the different incident light intensities of the 2 different irradiation sources. Sixteen fluorescent tubes Cleo-Performance R40W Philips of the DSSR emitted 0.23 mM photons l⁻¹ min⁻¹, while the Osram HBO 500 W of the LSSR emitted only 0.0814 mM photons l⁻¹ min⁻¹. Nevertheless, the irradiated surface area of the LSSR was much smaller than that of the

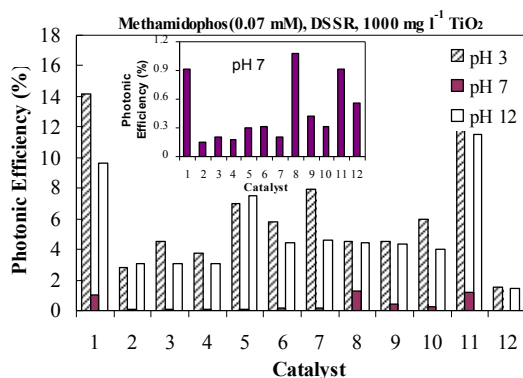
DSSR. Similar to the case with the LSSR, Cat 12 (Bayoxide T2) had the lowest photonic efficiency $\zeta = 0.04\%$. The photocatalytic degradation of Me more effective when using the DSSR than that using the LSSR because the illuminated surface area of the DSSR were much larger than that of the LSSR, which was a small glass plain quartz window. Moreover, the lamps of the DSSR emitted broad intensive bands of UV radiation at wavelengths from 310 to 380 nm, while the lamp of the LSSR emitted mainly at wavelength of 350-370 nm. Therefore it was not surprising that the photoactivity of used photocatalysts depends strongly on these different irradiation conditions.

At pH 3 and 12 (**Fig. 2a**), the photonic efficiency increased steeply in comparison with the LSSR. The highest value of $\zeta = 14.1\%$ was reached with Cat 11 at pH 12, followed by Cat 1 at pH 3 ($\zeta = 9.27\%$).

The photonic efficiency of most of 12 catalysts at pH 7 (**Fig. 2a**) increased by a factor from 1.05 by Cat 3 (Millennium PC 100) to 3.33 by Cat 8 (Mikroanatas) when the concentration of TiO₂ increased to 1000 mg l⁻¹. At a concentration of 1000 mg l⁻¹, Cat 8 showed a large photocatalytic activity with both the LSSR and DSSR for the degradation of Me. At pH 7, Cat 8 reached a photonic efficiency $\zeta = 1.58\%$ with the LSSR and $\zeta = 1.1\%$ with the DSSR. At pH 3 at a concentration of 1000 mg l⁻¹ (**Fig. 2b**), Cat 1 reached the highest photonic efficiency with $\zeta = 16.2\%$, followed by Cat 11 with $\zeta = 10.5\%$.



a) Concentration of catalyst : 500 mg l⁻¹



b) Concentration of catalyst : 1000 mg l⁻¹

Figure 2: Photonic efficiency of different catalysts in the degradation of methamidophos using the DSSR at pH 3, 7, and 12

3.2. Degradation of Mo: Effects of pH, catalysts concentration and type

At pH 7 and a concentration of 500 mg l⁻¹ TiO₂, the degradation of Mo using the DSSR was considerably faster than that using the LSSR. The highest photonic efficiency was reached by Cat 11 at $\zeta = 2.94\%$, followed by Cat 1 at $\zeta = 1.90\%$. The degradation half-life was only 4.6 min when using Cat 11 and was 7.1 min with Cat 1. The photonic efficiency of Cat 10 (Pt-P25) was unexpectedly low and was similar to that of Cat 2 (Millennium PC 50), Cat 8 (Mikroanatase), and Cat 9 (TCI Transcommerce). While Cat 8 with concentration of 1000 mg l⁻¹ was the most effective catalyst in the degradation of Me at pH 7, it was a poor catalyst in the degradation of Mo. Hence this again showed that the photocatalytic activity of the catalyst depended strongly on the organic pollutant. When the experiments were carried-out at pH 3 and 12 (Fig. 3a), the photonic efficiency of Cat 11 increased only slightly to 1.09 and 1.04 times, while

with Cat 8, ζ rose quickly by a factor of 10.13 and with Cat 2 by 8.52 at pH 3.

As observed in the degradation of Mo with the LSSR, when the concentration of TiO₂ increased from 500 to 1000 mg l⁻¹, the photonic efficiency of some catalysts did not rise significantly. It can be concluded that for some catalysts and organic pollutants, when concentrations increased the recombination process of the electron/hole pair dominates. The results are shown in Fig. 3b.

The achieved results from the photocatalytic detoxification of Me and Mo using the LSSR and DSSR revealed highly effective photocatalysts as well as demonstrated the feasibility of applying the DSSR in practice, especially in sun-rich countries, including Vietnam. Dillert et al was installed a pilot plant based on the DSSR for biologically pretreated industrial wastewaters in the Wolfsburg factory (Volkswagen AG). The DSSR exhibits specific advantages compared with the 2 other solar reactors: the parabolic trough reactor and the thin film fixed bed reactor.

The DSSR has low investment costs due to its simple construction; it can use the total global UV-irradiation, and its mass transfer is not limited. However, many disadvantages such as the low optical efficiency, the needed separation of TiO₂ from the purified water, the necessary large reactor area and oxygen supplying, and an addition of H₂O₂ for the purification of large waste water volumes, can hinder the broad extensive application of this reactor in practice. Beside the optimal modified catalyst Cat 11 (Pt-Hombikat UV100), the well-known catalyst P25 Degussa (Cat 1) still shows its high photonic efficiency in the degradation of Me and Mo.

4. CONCLUSIONS

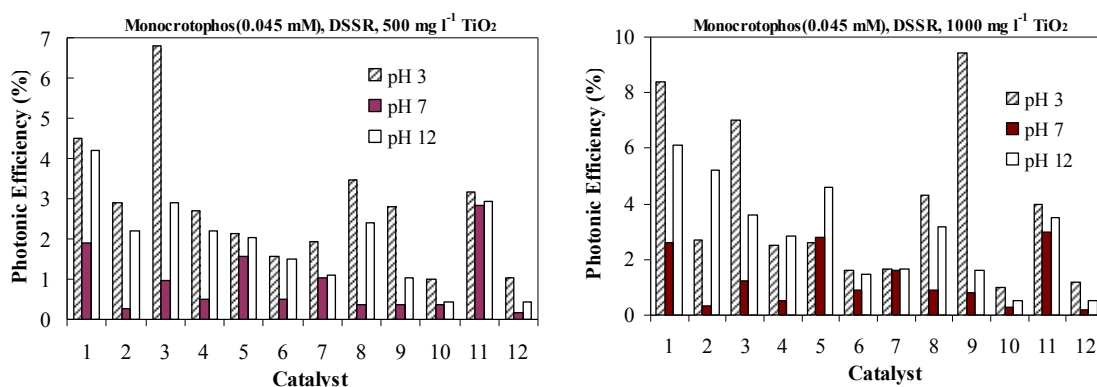
Using the DSSR at pH 7 and 500 mg l⁻¹ catalyst for the detoxification of Me, the highest values of ζ was reached with Cat 1 (P25 Degussa) at 0.81 %, whereas the value

increased to 1.1 % with Cat 8 (1000 mg l⁻¹ concentration). For the detoxification of Mo, the corresponding highest values of ζ = 2.94 % and 3.01 % were reached with Cat 11. The lowest photonic efficiency was achieved with Cat 12 (Bayoxide T2). The novel Cat 5 supplied by Millennium (PC 500) was also an effective catalyst. In both acidic and alkaline media (pHs 3 and 12), the photocatalytic degradation of Me and Mo was much faster than that at pH 7, where the degradation rate increased around 10 fold even when some low effective catalysts at pH 7 were used.

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a) Concentration of catalyst : 500 mg l⁻¹

b) Concentration of catalyst : 1000 mg l⁻¹

Figure 3: Photonic efficiency of different catalysts in the degradation of monocrotophos using the DSSR at pH 3, 7, and 12

REFERENCES

1. Nhan, D.D., Am, N.M., Hoi, N.C., Dieu, L.V., Carvalho, F.P., Villeuneve, J.P.,

Cattini, C., (1998) Organochlorine pesticides and PCBs in the Red River

Delta, North Vietnam, Marine Pollution Bulletin. 36 742-749.

2. Nhan, D.D., Am, N.M., Carvalho, F.P., Villeuneve, J.P., Cattini, C., (1999) Organochlorine pesticides and PCBs along the coast of North Vietnam, *The Science of the Total Environment*. 237/238 363-371.

3. Nhan, D.D., Carvalho, F.P., Am, N.M., Tuan, N.Q., Yen, N.T.H., Villeuneve, J.-P., Cattini, C., (2001) Chlorinated pesticides and PCBs in sediments and molluscs from freshwater canals in the Hanoi region, *Environmental pollution*. 112 311-320.

4. Quyen, P.B., Dan, D.N., Nguyen, V.S., (1995) Environmental pollution in Vietnam: analytical estimation and environmental priorities, *Trends in Analytical Chemistry*. 8 383-388.

5. Iwata, H., Tanabe, S., Sakai, N., Nishimura, A., Tasukawa, R., (1994) Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implication for global redistribution from lower latitudes, *Environmental Pollution*. 85 15-33.

6. Naylor, R.L., (1994) Herbicide Use in Asian Rice Production, *World Development*. 22 55-70.

7. Hussain, M. A., (1987) Anticholinesterase Properties of Methamidophos and Acephate in Insects and Mammals, *Bull. Environ. Contam. Toxicol*. 38.

8. Tomlin, C., (1994) *The Pesticide Manual*, Tenth Edition, Crop Protection Publications. British Crop Protection Council and Royal Society of Chemistry.

9. Doanh, B. S., Situation of using Plant Protective Agents (PPAs) in Vietnam and residue of PPAs in soils, waters and in agricultural products. Report at the Conference "Management of Plant Protective Agents in Vietnam"

10. Bahnemann, D.W., Bockelmann, D. and Golisch, R., (1991) Solar Energy Mater. 24 564 – 583.

11. Rauer, S., (1998) Untersuchung von kommerziell erhältlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivität. Diplomarbeit. Fachhochschule Hannover, Fachbereich Maschinenbau.